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LOCAL CRYSTALLIZATION OF GLASSES AIDED BY COPPER VAPOR LASER

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It is shown that a copper vapor laser can be used effectively for local crystallization of glasses with precipitation of active phases on a surface or in the interior volume of glass depending on its composition. A procedure is proposed for using a laser beam to form nanostructural waveguides with broadband near-IR luminescence peaking at 1300 – 1450 nm in glass with composition (mol.%) 7.5 Li_2O, 2.5 Na_2O, 20 Ga_2O_3, 35 GeO_3 and 35 SiO_2 doped with 0.1 – 0.5% NiO. A mechanism of self-limited laser heating, impeding subsequent growth of the nanocrystals formed, is demonstrated. The results of the investigations are of interest for developing active elements of integrated optics.

Key words: laser crystallization, gallium-germanium-silicate glasses, copper vapor laser.

For many centuries the crystallization of glass was viewed, first and foremost, as an adverse phenomenon that complicates the technological process of glass production, until in the mid-20th century the pioneering works of S. D. Stookey [1] led to the development of a new class of promising glass ceramic materials, referred to in the Russian literature as sitals, a term introduced by I. I. Kitaigorodskii. Right after the materials obtained by volume crystallization of glass methods were developed for directed surface crystallization of glass with precipitation of active crystalline phases, making it possible to obtain transparent oriented crystalline layers on a glass surface [2] and crystalline textures of large thickness [3].

Progress in microelectronics and laser technologies in the last decade with a general trend toward miniaturization of electronic devices led to active development of integrated optics, which required developing an adequate elemental and materials science base. Since glass remains, like in the past, a critically important material for optical technologies, in solving this problem more and more methods of local modification of glasses with formation of functional microstructures are being developed. Important examples are the methods of laser modification of glass [4], making it possible to form channel waveguides, Bragg lattices, elements of waveguide amplifiers, lasers and so on in glass. The natural development of this approach, which, however, required special research, became local crystallization of glass by a focused laser beam, first demonstrated at the end of the 1990s [5] and subsequently developed by T. Komatsu and his group (a large part of them is reviewed in [6]). The main objects for such research are glasses in which crystalline phases with promising properties from the standpoint of photonics and optoelectronic technologies, e.g. a large optical nonlinearity and large electro-optic coefficient, can easily precipitate.

As a rule continuous-wave near-IR lasers are used for local crystallization of oxide glasses, and a component absorbing radiation at the wavelength of the laser used, as a rule, a rare-earth or transition metal ion, is introduced into the glass. In a number of cases far-IR or UV lasers, whose radiation is strongly absorbed by practically all oxide glasses, are used. In using femtosecond lasers the absorption of the laser beam is of a multiphoton character and, thus, likewise, light energy is transferred to matter by means resonances in the UV range.

A pulsed copper vapor laser (CVL), emitting in the yellow-green region of the visible range at wavelengths 510.6 and 578.2 nm (green and yellow lines, respectively), was

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used in previous works for problems of laser crystallization. Explosive surface crystallization of glasses of the lanthanum-boron-germanate system near stoichiometric composition $LaBGeO_5$ was demonstrated with such a laser. Chromium oxide [7] or neodymium oxide [8] was used as the additive absorbing the laser radiation. This method makes it possible to grow in several seconds well formed and uniformly arranged crystals with a narrow size distribution, giving a SHG signal and, according to XPA data, having a stilwellite structure (Fig. 1), in the laser scanning direction along the surface of the glass. The dimensions of the crystals can change in the range 2 – 10 μm, depending on the irradiation regime. It was demonstrated that a CVL is especially effective for local heating of the glass containing neodymium, owing to the fact that both lines of the CVL coincide with the strong absorption bands of the Nd^{3+} ions. Together with pre-heating of the glass, directed toward decreasing the thermal stresses and preserving the wholeness of the sample, this circumstance made it possible to lower the molar content of neodymium oxide to 1%, required for quite intense absorption of CVL radiation, obtaining local crystallization in glass with the composition 1 Nd_2O_3, 24 La_2O_3, 25 B_2O_3 and 50 GeO_2, while previously 5 mol.% Nd_2O_3 had to be introduced into similar glass in order to solve the same problem with a continuous-wave titanium-sapphire laser (800 nm) [9].

There now exist tens of publications devoted to local crystallization of ferroelectrics and ferroelastics possessing high quadratic optical susceptibility, but much less attention has been devoted thus far to the formation of crystals that would affect the luminescence properties of a material. In some cases a change in the luminescence spectra was used as an indicator of crystallization, for example, with the formation of LaF_3 and CaF_2 nanocrystals in the interior of oxyfluoride glasses due to a change in the luminescence properties of Er^{3+} [10] or Nd^{3+} [11] ions that migrated in the nanocrystals. In silicate glass doped with nickel and erbium ions it was possible to precipitate in prescribed sections using a femtosecond laser LaF_3 and Ga_2O_3 nanocrystals into which Er^{3+} and Ni^{2+} ions migrated, initiating near-IR luminescence [12].

Not so long ago the well-known effect where broadband near-IR luminescence of Ni^{2+} ions arises when the ions are transferred from glass into heat-treatment formed nanocrystals with spinel structure based on gallate phases (Ga_2O_3 or $LiGa_5O_8$) was also demonstrated for germanium silicate glasses [13, 14]. A successful choice of glass-forming system and optimization of the composition for these glasses made it possible to lower the melting temperature to 1480°C (by at least 100°C relative to purely silicate glasses) [13] and to obtain optically uniform samples. The combination of good technological properties with local laser nano-structuring opens prospects for developing broadband near-IR optical amplifiers based on them.

In the present work it was shown for one of the compositions of the germanium-silicate system which were proposed in these studies [13, 14] that local nano-structuring of glass by means of laser radiation forming luminescing waveguides in glass that does not luminesce in the IR range in the uniform state is possible. The following glass composition was chosen for the experiments (mol.%): 7.5 Li_2O, 2.5 Na_2O, 20 Ga_2O_3, 35 GeO_2 and 35 SiO_2. Pure glass with this composition as well as glass doped with 0.1, 0.3 and 0.5 mol.% NiO (GGS-0, GGS-0.1, GGS-0.3 and GGS-0.5, respectively) were made. Chemically pure Li_2CO_3, Na_2CO_3, Ga_2O_3, GeO_2 and amorphous SiO_2 and NiO were used as initial materials. The glass was heated in a platinum crucible at 1480°C for 40 min to final mass 20 g, poured on a metal plate and pressed with another plate. The samples were made in the form of plane-parallel plates about 2 mm thick, whose surface was ground and polished. The glass containing no NiO was colorless, while the other glasses had a yellow-orange color, whose intensity increased together with the nickel oxide content.

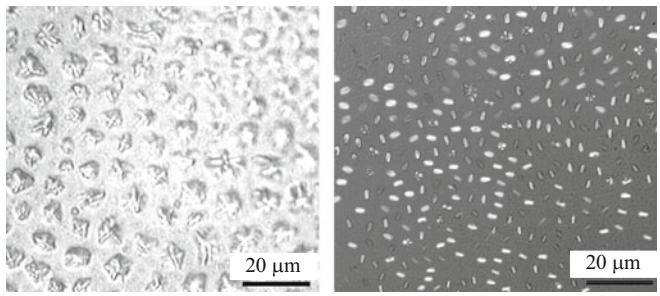

Fig. 1. Examples of surface sections of the glasses (mol.%) 0.05 Cr_2O_3, 25 La_2O_3, 25 La_2O_3, 50 GeO_2 (right) and 1 Nd_2O_3, 24 La_2O_3, 25 La_2O_3, 50 GeO_2 (left), on which single crystals with stilwellite structure were formed with a CVL.

A CVL emitting at 510.6 and 578.2 nm with average total power 5.5 W, pulse repetition frequency about 13 kHz and pulse duration 10 nsec was used for local crystallization of the samples. The optical scheme of the laser is described in detail in [15]. The arrangement of the setup is shown in Fig. 2. In the course of irradiation a sample was heated on a quartz-glass substrate in a miniature furnace with automatic temperature control near the top surface of the sample to prevent cracking under thermal stresses. In a number of experiments the chamber with the sample was closed with a glass top to decrease the temperature gradient inside the sample. The laser beam was focused inside the sample. The furnace with the experimental sample was placed on a two-coordinate motorized table, which could move in a plane perpendicular to the laser beam, with velocity from 25 to 200 μm/sec.

A DRON-3 (CuK_α radiation, Ni filter) diffractometer was used to confirm the x-ray amorphousness of the initial glass and to study the crystalline phases precipitated in the course of the experiment. The crystalline phases were identified by comparing the diffraction patterns with data in the JCPDS electronic database with x-ray data. The transmission spectra in the spectral range 280 – 900 nm were measured

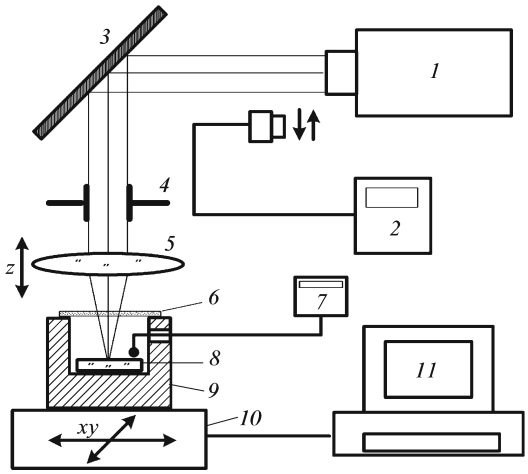

Fig. 2. Experimental arrangement of laser glass-treatment setup based on CVL: *1*) laser; *2*) optical power meter; *3*) mirror; *4*) diaphragm; *5*) condensing lens; *6*) glass top; *7*) furnace control block with automatic temperature control; *8*) sample; *9*) furnace; *10*) *xy* table; *11*) computer with table control software.

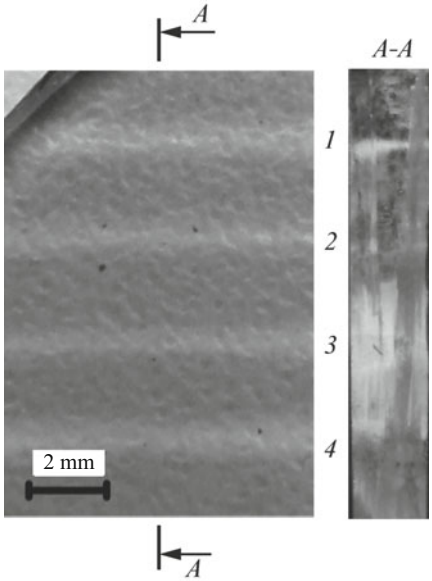

Fig. 3. GGS-0.3 glass sample irradiated with a CVL at temperature 562 ± 2°C and different beam scanning rates: *1*) 25 μm/sec; *2*) 50 μm/sec; *3*) 100 μm/sec; *4*) 200 μm/sec (top view of sample and side view on a polished section).

with a Cintra 303 dual-beam spectrophotometer. The refractive index was measured with a Metricon 2010 refractometer at wavelength 633 nm. The luminescence spectra were recorded using a MDR-23U diffraction monochromator with a detector based on an InGaAs p-i-n photodiode (Hamamatsu G10899, cut-off wavelength 1.7 μm) in the wavelength range 800 – 1800 nm with excitation at the wavelength 405 or 532 nm.

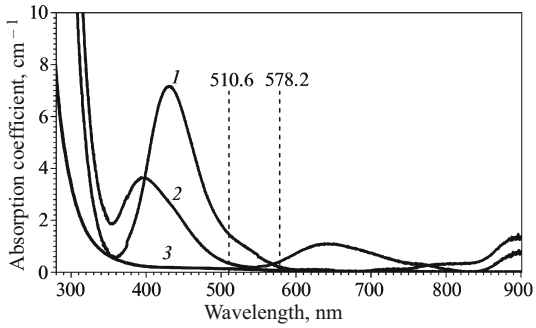

Fig. 4. Absorption spectra of GGS-0.3 glass outside (*1*) and inside (*2*) the irradiated region and absorption section of GGS-0 (*3*) glass.

In some cases, where the temperature of the samples was quite close to vitrification temperature (t_g = 570°C), the laser irradiation of the doped nickel oxide glasses changed the color of the irradiated region from orange to sky-blue, which was accompanied by a change in the refractive index of the glass, with the transparency remaining unchanged (Fig. 3). Above t_g the sample started to stick to the substrate, while below 540°C the irradiation sections did not change color, demonstrating only a change in the refractive index. When the sample was irradiated without the top the vertical temperature gradient caused the width of the sky-blue bands closer to the bottom, hotter part of the sample to increase. However, conversely, when a top was used the bands became narrower closer to the bottom surface of the sample: evidently, as the temperature gradient decreased, a drop in the intensity of the laser radiation passing through the sample started to play a decisive role. The samples of nickel-free GGS-0 glass did not show any visible changes under irradiation. The absorption spectra of the glass inside and outside the irradiated region (see Fig. 4) are very close to those of uniform glass and glass nano-structured by heat-treatment in a furnace, during which the Ni^{2+} ions became embedded in the nanocrystals formed with spinel structure [14]. However, it should be noted that for laser-irradiated samples the absorption coefficient is an average quantity, since in connection with the variable width of the sky-blue region over depth in the sample glass regions whose color did not change could also have been partially present in the beam at the time the transmission spectrum was recorded. Just as in the case of volume nano-structuring, the glass sections whose color did change exhibit broadband luminescence in the region 1150 – 1700 nm peaking at 1300 – 1450 nm depending on the excitation wavelength, while the initial glass does not luminesce in this range (Fig. 5). Analysis of the x-ray diffraction patterns (Fig. 6) shows the presence of crystal embryos even in the initial glass and growth of Ga_2O_3 crystals with spinel structure under laser irradiation. The good agreement between the optical and x-ray data shows that the same nano-structuring processes occur in the laser-irradiated region of the glass as with heat-treatment. The large width of the peaks

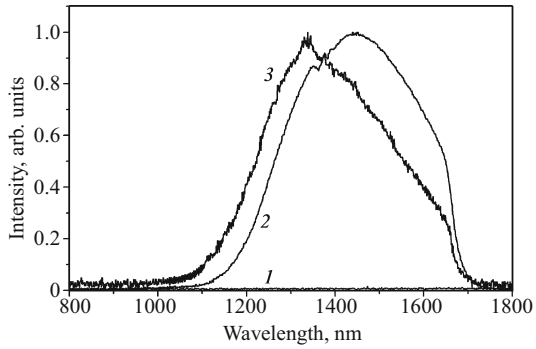

Fig. 5. Luminescence spectra of GGS-0.3 glass: *1*) unirradiated glass, excitation at wavelength 405 mm; CVL irradiated section under excitation at wavelengths 405 (*2*) and 532 nm (*3*).

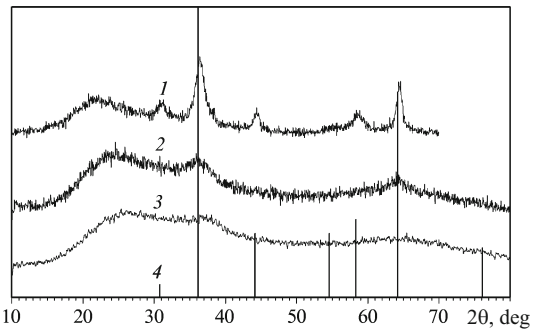

Fig. 6. X-ray diffraction pattern of GGS-0.1 glass: *1*) glass heat-treated in a furnace at 690°C for 18 h; *2*) laser-irradiated section of the initial glass; *3*) initial glass; *4*) line diffraction pattern of crystalline Ga_2O_3 (card No. 20-0426 in the JCPDS database).

(Fig. 6, curve *2*) attests to very small size of the laser-formed crystals, which, drawing an analogy with the data in [14], can be estimated to be 6 – 8 nm. With prolonged soaking for 18 h at 690°C in a furnace (Fig. 6, curve *1*) the sizes and content of the Ga_2O_3 crystal increase, but the glass ceramic material loses transparency.

The practically identical parameters of the bands formed with scan rates differing by a factor of 8 are very interesting results (see Fig. 3). In all probability, this is explained by a sharp drop of the absorption of the glass at the CVL wavelengths as nickel migrates into the nanocrystals. Thus, owing to the favorable correlation of the absorption spectra and the CVL wavelengths there arises a unique mechanism of self-limitation of the laser-heating process after nanocrystals appear that prevents the crystals from growing wildly and gives definite freedom in choosing the irradiation regimes. Another important result is an appreciable increase of the refractive index in the irradiated region. Refractometry showed that the refractive index in the irradiated region of the GGS-0.5 sample grew by 0.006 – 0.008 (for initial value 1.6249 ± 0.0004 at 633 nm). This shows that a waveguide effect is possible, which makes it possible to use the nanostructured channel formed in the glass as a waveguide luminescing in the near-IR region.

In summary, it has been shown that a CVL is an effective tool for local heating and crystallization of glass, and depending on the composition both surface (as in lanthanum-boron-germanate glasses) and volume (as in GGS glasses) crystallization are possible. In addition, in the latter case, owing to the felicitous combination of the optical properties of Ni^{2+} ions and the CVL wavelengths a self-limiting heating mechanism is realized, which makes it possible to easily obtain nano-crystalline structures, preserving the transparency of the glass. In addition, it becomes possible to create local structures with broadband and IR luminescence in glass that does not exhibit IR luminescence. The waveguides formed in this manner are of great interest for developing active elements for integrated optics.

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